

# PATENT SPECIFICATION

(11) 1409594

1409594

- (21) Application No. 13403/73 (22) Filed 20 March 1973  
 (31) Convention Application No. 2214293 (32) Filed 24 March 1972  
 (31) Convention Application No. 2236575 (32) Filed 26 July 1972 in  
 (33) Germany (DT)  
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 B2E 18Y 207 209 23Y 299 319 339 33X 398 44Y 473  
 485 498 510 51X 533 537 53Y 543 545 546 547  
 565 566 567 56Y 608 65Y 708 720 72X 743  
 747 74Y 753 755 756 757 775 776 777 77Y  
 79X 804

## (54) ADHESIVE COMPOSITIONS

(71) We, BEIERSDORF AKTIEN-GESELLSCHAFT, a German Company of 2000 Hamburg, 20, Unnastrasse 48, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to adhesive compositions. In particular, the invention relates to pressure sensitive adhesive compositions which may be applied as aqueous pastes, have good quick stick characteristics to provide prolonged adherence at room temperature, are resistant to cold flow, have good resistance to aging, and are suitable in particular for use in the manufacture of self-adhesive labels which adhere well to the most varied materials but which can easily be removed therefrom with water.

Articles of glass, porcelain, metal and plastics material, coated or uncoated, are often provided in warehouses with characterising labels which adhere so well that they can be removed with great difficulty from the articles without leaving residues of the label on the article; the article. Furthermore, the substrate material of the label is part of the article. Also, the identifying material of many types of material described in

[Price 33p]

in order that they can be readily removed without a residue. This form of label is particularly used in warehouses and self-service stores using labelling devices; the device is used to stick for example labels having a price impression to the article in question. In order to prevent a purchaser with intent to defraud exchanging a price label on an expensive article with one on a less expensive article, such labels (which are conventionally coated with a water insoluble self-adhesive material) are usually provided with special cutting lines in the form of an interrupted wavy line or the like or provided with weakening lines or zones. These lines or zones cause the label to be torn if an attempt is made to remove it. However, to form cutting, stamping or weakening lines or zones in each individual label on a label strip, substantial additional manufacturing steps are required.

In prior pressure sensitive adhesive marking labels there has been great difficulty in providing both good adhesion to articles of various types of material (i.e. broad usability)

## ERRATA

SPECIFICATION No. 1,409,594

Page 3, line 17, for the read then  
 Page 5, line 7, for 80% (second occurrence)  
 read 8%.

THE PATENT OFFICE  
 14th November, 1975

# PATENT SPECIFICATION

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## (54) ADHESIVE COMPOSITIONS

- (71) We, BEIERSDORF AKTIEN-GESELLSCHAFT, a German Company of 2000 Hamburg, 20, Unnastrasse 48, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to adhesive compositions. In particular, the invention relates to pressure sensitive adhesive compositions which may be applied as aqueous pastes, have good quick stick characteristics to provide 15 prolonged adherence at room temperature, are resistant to cold flow, have good resistance to aging, and are suitable in particular for use in the manufacture of self-adhesive labels which adhere well to the most varied 20 materials but which can easily be removed therefrom with water.
- Articles of glass, porcelain, metal and plastics material, coated or uncoated, are often provided in warehouses with character- 25 ising labels which adhere so well that they can be removed from the article only with great difficulty. When the label is removed from the article to which it adhered, often residues of adhesive remain on the article, or 30 the label itself tears leaving part thereof on the article; thus necessitating cleaning of the article. Furthermore when such labels are removed there is a danger that part of the substrate may adhere to the label removed. 35 This is particularly the case if the substrate consists of a sensitive and flaky material.
- Also, there is wide use of self-adhesive identifying labels which adhere to articles of many types of materials or of a single type 40 of material much less strongly than the labels described above. These labels are provided in order that they can be readily removed without a residue. This form of label is particularly used in warehouses and self-service stores using labelling devices; the device is used to stick for example labels having a price impression to the article in question. In order to prevent a purchaser with intent to defraud exchanging a price label on an expensive article with one on a less expensive article, such labels (which are conventionally coated with a water insoluble self-adhesive material) are usually provided with special cutting lines in the form of an interrupted wavy line or the like or provided with weakening lines or zones. These lines or zones cause the label to be torn if an attempt is made to remove it. However, to form cutting, stamping or weakening lines or zones in each individual label on a label strip, substantial additional manufacturing steps are required.
- In prior pressure sensitive adhesive marking labels there has been great difficulty in providing both good adhesion to articles of various types of material (i.e. broad usability) and also easy subsequent removal.
- The present invention provides an adhesive composition which will enable pressure sensitive identification labels to be made which have good long term adherence characteristics for articles of various materials. Further such labels tend, when the labels are removed from the article carrying them, to tear, notwithstanding that they have e.g. no cutting or weakening lines. However, such labels may be easily removed from the carrying article without tearing or leaving a residue on treatment with water or a washing solution after a short softening time.
- It has now been found that this advantageous combination of properties can be

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obtained if label paper or other sheet materials, e.g. cloth, plastics foils or non-woven fabrics is coated with a water soluble pressure sensitive adhesive of a quite particular composition.

According to the present invention there is provided an adhesive composition which comprises an aqueous mixture of

(a) acrylic acid ester copolymer, which copolymer contains 80—90% by weight of units derived from one or more acrylic acid alkyl esters containing 4 to 12 carbon atoms in the alcohol residue and 10—20% by weight of units derived from one or more copolymerisable monomers, and/or water-insoluble polyvinyl alkyl ether in dispersed form;

(b) polyvinylmethylether;

(c) an alkali metal and/or ammonium salt of polyacrylic acid, of polymethacrylic acid or of a copolymer of acrylic and methacrylic acids;

(d) a monomeric plasticiser and

(e) an emulsifying agent.

The present compositions may be prepared by mixing an aqueous dispersion of component (a) with components (b) to (e).

The proportions of the components forming the mixture can be varied within a wide range, which can simply be determined by straight forward tests. In practice the type and amount of component should be chosen such that the adhesive does not penetrate the envisaged carrier material and which, after drying, gives a layer of good adhesive power and good dispersability.

The copolymerizable monomer in the acrylic acid ester copolymer of component (a) is preferably acrylic acid, methacrylic acid, acrylonitrile, vinyl acetate, 2-ethylhexylmaleate, diethyl maleate or methacrylic acid methyl ester or a mixture of one or more of these.

Most preferably, the acrylic acid ester copolymers are manufactured by polymerisation of 80—90% by weight of 2-ethylhexylacrylate or n-butylacrylate with 10—20% by weight of acrylic acid, methacrylic acid, acrylonitrile, vinyl acetate, 2-ethylhexylmaleate, diethyl maleate and/or methacrylic acid methyl ester. Particularly advantageous are such copolymers which contain 2 to 10% by weight acrylic acid. The acrylic acid ester copolymers, useable in the invention, are known products obtainable in commerce or can be readily manufactured according to known polymerisation processes.

Even though in particular cases a single acrylic acid copolymer can be used in the mixture, it has nonetheless been shown that in most practical embodiments of the invention, particularly for adhesives for use in the manufacture of labels, it is better to use two acrylic acid ester copolymers having differing properties; one consisting of an uncross-

linked acrylic acid ester copolymer and the other of a corresponding copolymer cross-linked e.g. by zinc acetate.

Preferably, the mixture contains, based on 100 parts by weight of the total solvent or diluent-free mixture:

25 to 35 parts by weight of cross-linked acrylic acid ester copolymer,

10 to 20 parts by weight of uncross-linked acrylic acid ester copolymer,

10 to 20 parts by weight polyvinylmethylether,

10 to 20 parts by weight alkali metal and/or ammonium salt of polyacrylic acid, polymethacrylic acid or a copolymer of acrylic and methacrylic acids,

10 to 20 parts by weight monomeric plasticiser and

10 to 15 parts by weight emulsifying agent.

In the adhesive composition of the invention, the weaker adhering cross-linked acrylic acid ester copolymer serves as a framework to give the adhesive good sheer strength (i.e. acts as a sheer resisting component), and the uncross-linked acrylic acid ester copolymer, which is as such a good pressure sensitive adhesive, gives the adhesive good quick stick and strong long term adhesion characteristics towards articles of various types (i.e. acts as the strongly adherent component).

As water-insoluble polyvinyl alkyl ethers, which can replace all or part of the acrylic acid ester copolymer in component (a), water insoluble polymers of vinylisobutyl ether and/or vinyl ethyl ether have been shown to be particularly suitable. These components are generally used in the form of aqueous dispersions obtainable in commerce in various viscosity grades and having solids content of 50 to 55% by weight. Alternatively the dispersions can be readily manufactured by known polymerisation processes. These polyvinyl ether dispersions of water insoluble polyvinyl ether are essentially different from the water soluble polyvinylmethylether also present in the adhesive composition.

Preferred as salts of polyacrylic acid, polymethacrylic acid or a copolymer of acrylic and methacrylic acids, which are all water soluble and which can serve as a framework-providing substance in the adhesive composition, are the sodium ammonium salt of a copolymer of acrylic and methacrylic acid (e.g. the commercial product "Silkoplex 1" of Röhm GmbH, Darmstadt, Silkoplex is a registered Trade Mark) and the sodium ammonium salt of polyacrylic acid. As well as these the sodium, potassium or ammonium salts of the noted polymers and copolymers can also be used.

Suitable as polyvinylmethyl ether for the adhesives according to the invention are water soluble compounds of consistency similar to soft resins, particularly those with a K value

- of about 40 (e.g. the commercial product "Lutonal M 40" of BASF—Lutonal is a registered Trade Mark). The polyvinylmethyl ether acts, in the adhesive composition as a tackifier and softener.
- As monomeric plasticiser (d), liquid plasticisers of oily consistency are suitable, particularly those on a phthalate basis (e.g. dioctyl phthalate, dimethylglycolphthalate).
- The emulsifying agent (e) added to the novel adhesive composition serves for redispersing acrylic acid ester copolymer and/or polyvinyl ether dispersions. Further it causes a pressure sensitive adhesive layer applied to a carrier using the composition to dissolve partially in water and to swell partially and the forms a colloidal solution. Particularly suitable for this purpose are non-ionic emulsifiers and stabilising agents such as fatty acid esters of polyhydric alcohols, ethoxylated phenols, polyvinyl alcohols and above all aromatic polyglycol ethers.
- The present invention also provides a method of preparing pressure-sensitive adhesive material which method comprises coating sheet material with a novel composition (after dilution if required) and drying the coating.
- Preferably the coating composition contains 40 to 60% by weight of the mixture of components (a) to (e). Suitably the composition is applied such as to provide a dried coating of 20–50 g/m<sup>2</sup> of sheet material. The sheet material may be paper. If desired siliconised (release) paper may be applied to the coated surface of the sheet material after drying. Alternatively the coating composition may be applied to siliconised (release) paper and, after drying, a further sheet material is applied to the coated surface and the adhesive layer is then transferred to the further sheet material by lamination.
- As a further embodiment the invention also provides pressure-sensitive adhesive sheet material wherein the sheet material is coated with a substantially dry mixture of
- acrylic acid ester copolymer, which copolymer contains 80 to 90% by weight of units derived from one or more acrylic acid alkyl esters containing 4 to 12 carbon atoms in the alcohol residue and 10–20% by weight of units derived from one or more copolymerisable monomers, and/or water-insoluble polyvinyl-alkylether;
  - polyvinylmethyl ether;
  - an alkali metal and/or ammonium salt of polyacrylic acid, of polymethylacrylic acid or of a copolymer of acrylic and methacrylic acids,
  - a monomeric plasticiser and
  - an emulsifying agent.
- The utility of the pressure-sensitive adhesive compositions according to the invention is not restricted to the manufacture of conventional labels. For example, labels or adhesive tapes can be made which consist of water-soluble paper, a water-soluble foil or a water-soluble non-woven fabric coated with the pressure sensitive adhesive composition. To avoid penetration of the sheet material however, it is usually necessary, in this case to provide the material, before coating with the pressure sensitive adhesive composition, with a water-soluble pre-coat (base layer) of polyvinyl alcohol and/or ethoxylated polyvinyl alcohol. The present compositions may also conveniently be used to coat strips of paper (e.g. crepe paper) which are particularly used in packaging and transporting of sanitary ware (e.g. basins or baths) to minimise damage.
- The following Examples further illustrate the present invention. In the Examples parts and percentages are by weight unless otherwise indicated and all dispersions are aqueous dispersions.

	Example 1 parts (solvent-and diluent-free)	Example 2 parts (solvent-and diluent-free)
90 Acrylate dispersion (copolymer of 90% acrylic acid n-butyl ester and 10% acrylic acid, cross-linked with zinc acetate) (viscosity of about 50% aqueous dispersion at 25°C: 1.1 poise)	30	30
95 Acrylate dispersion (copolymer of 90% n-butylacrylate and 10% acrylic acid) (viscosity of about 50% aqueous dispersion at 25°C: 1.1 poise)	20	10
100 Polyvinylmethylether (K value about 40) ("Lutonal M 40", BASF)	20	15

	Example 1 parts (solvent-and diluent-free)	Example 2 parts (solvent-and diluent-free)
5 Sodium ammonium salt of a copolymer of acrylic and methacrylic acids ("Silkoplex 1", Rohm GmbH)	10	20
Monomeric plasticiser (di-octylphthalate)	10	15
10 Non-ionic emulsifying agent (aromatic polyglycoether) ("Emulvin-W", Bayer-Emulvin is a registered Trade Mark)	10	10

The individual components were mixed together in any desired order in a suitable stirring vessel using a stirrer with slow stirring without difficulty. The stirring in of the emulsifying agent is preferably carried out with care and particularly slowly in order to avoid foam formation and air inclusion.

The pasty pressure-sensitive adhesive composition obtained, which can be adjusted by suitable dilution with water to a concentration of components (a) to (e) of 40 to 60%, is used for the manufacture of labels using customary coating apparatus, e.g. by roller coating in combination with a doctor blade or by bar coating. The composition is applied such that, after drying at 100 to 150°C in a step-wise heating drying channel, the label paper carries a coating of 20 to 50 grams/m<sup>2</sup>. At the end of the drying channel the dried pressure-sensitive adhesive layer on the label paper is coated with siliconised release paper.

According to another process, the adhesive composition is applied to siliconised parchment paper (release paper) at the same coating thickness and at the end of the drying channel the label paper is laminated on to the adhesive layer on the siliconized paper (transfer process). The so obtained label base material can then be cut up in conventional manner in a stamping station by two subsequently arranged separate stamping devices, in the longitudinal and cross-directions, to form individual labels in known manner. In each case the paper sheet and the underlying adherent layer are cut through, but the siliconised release paper is not cut through. The latter serves as a carrier (cover) for the pressure-sensitive adhesive labels which are initially adherent thereto and remain so until use.

The so manufactured pressure-sensitive adhesive labels show good quick stick properties, adhere well to articles of for example glass, porcelain, wood, metal, various plastics and card. Further the labels tear when

attempt is made to remove them from the article with splitting of the label material thus hindering exchange of labels, for purposes of fraud, even though no special treatment step, e.g. cutting, stamping, or application of weakening of lines or zones or the like has been performed. Moreover, the new labels can easily be removed without residue by treatment with water or a washing solution after a short softening time (e.g. 2 to 5 minutes).

### Example 3

	Parts (solvent-and diluent-free)	
Acrylate dispersion (copolymer of 45% 2-ethylhexylacrylate, 45% n-butylacrylate, 3% vinylacetate and 7% acrylic acid, cross-linked with zinc acetate)	30	75
Acrylate dispersion (copolymer of 45% 2-ethylhexylacrylate, 45% n-butylacrylate, 3% vinylacetate and 7% acrylic acid, uncross-linked)	20	80
Polyvinylmethylether (K value about 40 "Lutonal M 40", BASF)	20	
Sodium ammonium salt of a copolymer of acrylic and methacrylic acids ("Silkoplex 1", Rohm GmbH)	10	85
Monomeric plasticiser based on dimethyl glycol phthalate ("Palatinol O", BASF)	10	90
Non-ionic emulsifier (nonylphenolpoly-glycoether) ("Arkopal N-110", Farbwerke Hoeschst)	10	

["Palatinol" and "Arkopal" are registered Trade Marks.] 95

Example 4		Example 6	
	Parts (solvent-and diluent-free)		Parts (solvent-and diluent-free)
5	Acrylate dispersion (copolymer of 80% 2-ethylhexylacrylate, 80% n-butylacrylate, 5% methacrylic acid methyl ester, 5% vinylacetate, 2% acrylic acid cross-linked with zinc acetate)	Polyvinylisobutylether dispersion (about 55% aqueous dispersion, viscosity at 25°C: 800 to 2500 cP (measured on Epprecht-viscosimeter type STV, C III) ("Lutonal I 60 D", BASF)	65
10			70
15	Acrylate dispersion (copolymer of 80% 2-ethylhexylacrylate, 8% n-butylacrylate, 5% methacrylic acid methyl ester, 5% vinylacetate, 2% acrylic acid, uncross-linked)	Polyvinylisobutylether dispersion (about 55% aqueous dispersion, viscosity at 25°C: 1500 to 2500 cP (measured in Epprecht-viscosimeter type STV, CIII) ("Lutonal I 65 D", BASF)	75
20	Polyvinylmethylether (K value about 40 "Lutonal M40", BASF)	Polyvinylmethylether (K value about 40) ("Lutonal M 40", BASF)	80
25	Sodium ammonium salt of a copolymer of acrylic and methacrylic acids ("Silkoplex 1", Röhm GmbH)	Sodium ammonium salt of a copolymer of acrylic and methacrylic acids ("Silkoplex 1", Röhm GmbH)	85
30	Monomeric plasticiser (dimethylglycolphthalate)	Monomeric plasticiser (dimethylglycolphthalate)	
35	Non-ionic emulsifier (aromatic polyglycolether) ("Emulvin-W", Farbenfbk. Bayer AG)	Non-ionic emulsifier (aromatic polyglycolether) ("Emulvin-W", Farbenfabriken Bayer AG)	
40	Example 5	Antioxidant (dioxydiphenylmethane derivative) (aging protection agent "ZKF", Farbenfabriken Bayer AG)	90
45	Acrylate dispersion (copolymer of 45% 2-ethylhexylacrylate, 45% n-butylacrylate, 3% vinylacetate and 7% acrylic acid, cross-linked with zinc acetate)		95
50	Polyvinylisobutylether dispersion (about 55% by weight aqueous dispersion, viscosity of 25°C: 800 to 2500 cP (measured on Epprecht-viscometer type STV, CIII) ("Lutonal I 60 D", BASF)		100
55	Polyvinylmethylether (K value about 40) ("Lutonal M40", BASF)		
60	Sodium ammonium salt of a copolymer of acrylic and methacrylic acids ("Silkoplex 1", Röhm GmbH)		
	Monomeric plasticiser based on dimethylglycol phthalate ("Palatinol O", BASF)		
	Non-ionic emulsifier (nonylphenolpolyglycolether) ("Arkopal N-110", Farbwerke Hoechst)		
	Antioxidant (dioxydiphenylmethane derivative) (aging protection agent "ZKF", Farbenfabriken Bayer AG)		

The pressure sensitive adhesive compositions of Examples 3, 4, 5 and 6 also show the same advantageous combination of valuable properties (good quick stick, exceptionally long term adherence to surfaces of various types, resistance to cold flow and aging, easy removal with water and aqueous preparations) as the compositions described in Examples 1 and 2. They can be used for the same purposes as described therein.

#### WHAT WE CLAIM IS:—

1. An adhesive composition which comprises an aqueous mixture of
  - (a) acrylic acid ester copolymer, which copolymer contains 80—90% by weight of units derived from one or more acrylic acid alkyl esters containing 4 to 12 carbon atoms in the alcohol residue and 10—20% by weight of units derived from one or more copolymerisable monomers, and/or water-insoluble polyvinylalkylether in dispersed form;
  - (b) polyvinylmethyl ether;
  - (c) an alkali metal and/or ammonium salt of polyacrylic acid, of polymethacrylic acid or of a copolymer of acrylic and methacrylic acids;
  - (d) a monomeric plasticiser and
  - (e) an emulsifying agent.

2. A composition according to claim 1 wherein, in component (a), the copolymerizable monomer in the copolymer is acrylic acid, methacrylic acid, acrylonitrile, vinyl acetate 2-ethylhexylmaleate, diethyl maleate or methacrylic acid methyl ester or a mixture of one or more of these.
3. A composition according to claim 1 wherein, in component (a), the acrylic acid ester copolymer consists essentially or exclusively of one or more copolymers comprising 80 to 90% by weight of 2-ethylhexyl acrylate or n-butylacrylate and 10 to 20% by weight of acrylic acid, methacrylic acid, acrylonitrile, vinyl acetate, 2-ethylhexyl maleate, diethyl maleate and/or methacrylic acid methyl ester.
4. A composition according to claim 3 wherein, in component (a), the acrylic acid ester copolymer contains 2 to 10% by weight acrylic acid.
5. A composition according to any one of claims 1 to 4 wherein, in component (a), the water-insoluble polyvinylalkyl ether is a polymer of vinylisobutyl ether and/or vinyl-ethyl ether.
6. A composition according to any one of claims 1 to 4 wherein the mixture contains, based on 100 parts by weight of the total solvent—or diluent-free mixture,
  - 25 to 35 parts by weight of cross-linked acrylic acid ester copolymer;
  - 10 to 20 parts by weight of uncross-linked acrylic acid ester copolymer;
  - 10 to 20 parts by weight polyvinylmethyl ether;
  - 10 to 20 parts by weight alkali metal and/or ammonium salt of polyacrylic acid, polymethacrylic acid or a copolymer of acrylic and methacrylic acids,
  - 10 to 20 parts by weight of monomeric plasticiser and
  - 10 to 15 parts by weight emulsifying agent.
7. A composition according to claim 1 substantially as described with reference to any one of the foregoing Examples.
8. A method of preparing pressure sensitive adhesive sheet material which method comprises coating sheet material with a composition according to any one of claims 1 to 7 and drying the coating.
9. A method according to claim 8 wherein components (a) to (e) constitute 40 to 60% by weight of the coating composition.
10. A method according to claim 8 to 9 wherein the composition is applied such as to provide a dried coating of 20—50 g/m<sup>2</sup> of sheet material.
11. A method according to any one of claims 8 to 10 wherein the sheet material is paper.
12. A method according to any one of claims 8 to 11 wherein siliconised paper is applied to the coated surface of the sheet material after drying.
13. A method according to any one of claims 8 to 11 wherein the coating composition is first applied to siliconised paper and, after drying, a further sheet material is applied to the coated surface and the adhesive layer is then transferred to the further sheet material by lamination.
14. Method according to claim 9 substantially as described in any one of the foregoing Examples.
15. Material prepared by the method claimed in any one of claims 8 to 14.
16. Sheet material coated with a substantially dry mixture of
  - (a) acrylic acid ester copolymer, which copolymer contains 80—90% by weight of units derived from one or more acrylic acid alkyl esters containing 4 to 12 carbon atoms in the alcohol residue and 10—20% by weight of units derived from one or more copolymerisable monomers, and/or water-insoluble polyvinylalkyl ether;
  - (b) polyvinylmethyl ether;
  - (c) an alkali metal and/or ammonium salt of polyacrylic acid, of polymethacrylic acid or of a copolymer of acrylic and methacrylic acids,
  - (d) a monomeric plasticiser and
  - (e) an emulsifying agent.
17. Material according to claim 16 wherein, in component (a), the copolymerizable monomer in the copolymer is acrylic acid, methacrylic acid, acrylonitrile, vinyl acetate, 2-ethylhexylmaleate, diethyl maleate or methacrylic acid methyl ester or a mixture of one or more of these.
18. Material according to claim 16 wherein, in component (a), the acrylic acid ester copolymer consists essentially or exclusively of one or more copolymers comprising 80 to 90% by weight of 2-ethylhexyl acrylate or n-butylacrylate and 10 to 20% by weight of acrylic acid, methacrylic acid, acrylonitrile, vinyl acetate, 2-ethylhexyl maleate, diethyl maleate and/or methacrylic acid methyl ester.
19. Material according to claim 18 wherein, in component (a), the acrylic acid ester copolymer contains 2 to 10% by weight acrylic acid.
20. Material according to any one of claims 16 to 19 wherein, in component (a), the water-insoluble polyvinyl alkyl ether is a polymer of vinylisobutyl ether and/or vinyl-ethyl ether.
21. Material according to any one of claims 16 to 19 wherein the mixture contains, per 100 parts by weight,
  - 25 to 35 parts by weight of cross-linked acrylic acid ester copolymer;
  - 10 to 20 parts by weight of uncross-linked acrylic acid ester copolymer;

- 10 to 20 parts by weight polyvinylmethyl ether, ;  
10 to 20 parts by weight alkali metal and/  
5 or ammonium salt of polyacrylic acid, polymethacrylic acid or a copolymer of acrylic and methacrylic acids,  
10 to 20 parts by weight monomeric plasticiser and  
10 to 15 parts by weight emulsifying agent.  
10 22. Material according to any one of claims 16 to 21 which carries 20—50 g/m<sup>2</sup> of the coating.  
23. Material according to any one of claims 16 to 22 having siliconised paper applied to 15 the coated surface.

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